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Defect studies using advances with ion beam excited luminescence

Peter D Townsend[a]*, Yafang Wang[b]

[a]University of Sussex, Brighton BN1 9QH, UK,
[b]School of Science, China University of Geosciences, Beijing, China 100083

Abstract

Luminescence techniques offer extremely sensitive probes of imperfections and structural changes in insulating materials. Among the many possible routes of signal excitation are the use of ion beams (IL) and the rarely used combination of ion beams with other excitation sources such as photons (PL), electrons (CL) or X-rays (RL). Ion beams can stimulate intrinsic signals as well as those from defect sites and control of the ion beam energy allows one to vary the depth of material that is being studied. Equally valuable is that variations in the excitation rate change the relative importance of signals from different types of luminescence site. Such flexibility in the excitation methods allows detailed quantification and identification of the structures which have been formed in irradiated material. Additional identification and separation of overlapping features is feasible by lifetime resolved luminescence, and/or by pulsing the ion beam. Ion beam coupled with other excitations can be used to probe defects via the luminescence characteristics of their excited states. Such combinations of IL with PL, CL or RL offer more insights than are possible with each technique independently. For the wide band gap insulators, such as sapphire or silica, the value of full spectral coverage in luminescence detection and photo-excitation will be emphasized, not least because from the optical absorption data it is evident that the simple defect structures become more complex in highly irradiated materials. Possibilities of resolving nanoparticle growth, amorphisation or new phases can all be addressed via the luminescence signals. A comment on systematic errors in data handling and processing is included.

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Key words: *Luminescence; ion beam luminescence; ion implantation*

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1. Introduction

There is a very long history of observations of luminescence from insulating and biological materials and improvements in experimental techniques have developed greatly over the last century. The inherent sensitivity and spectral information is useful for studies of imperfections and defect sites in insulators (and semiconductors) it offers the ability to subtly discriminate between different materials. Therefore it has appealed not only to physicists [1-5], but also mineralogists and geologists [6-12] as well as to other scientists [13-17]. More recently, luminescence has found an increasing role in medical applications such as optical routes to detect different types of cancer, disease and tooth decay. Such a long and varied history spans detection from colour film to spectral records using photomultiplier tubes (PM) and CCD detectors. There are some negative consequences of this wide appeal and very long experimental history as the early data were often recorded in non-quantitative fashions and, for example, the spectrally resolved information initially appeared on chart paper directly from a monochromator recording. These early results preceded modern computer data logging and the essential corrections for the spectral responses of the system (monochromator and PM tube etc) had to be made manually. Consequently many publications just used the raw data. This, together with incorrect handling of the subsequent signal processing for analysis, has meant that there are many subsets of the luminescence community who are making systematic errors. Some of these problems will be mentioned. However, the objective here is to emphasise the benefits of using ion beam excited luminescence (IL). This will appeal to experts of ion beam technologies, but such users may not necessarily be skilled in luminescence procedures, so discussion of correct signal processing is relevant.

The science of the luminescence process is encapsulated neatly by a configurational co-ordinate diagram (figure 1) in which an electron is trapped in a potential well. One can specify the potential energy and a distance parameter relative to some reference point site, such as the centre of the well. For example there may be a vacancy in a crystal lattice and the electron is in an energy box formed by the neighbours. Thermal energy offers access to higher states within this parabolic energy well. Excitation energy can raise the electron to a higher level and generally this upper parabola is shallower and displaced further from the reference point. Hence the recovery to the ground state involves a lower energy transition than for the excitation. It further implies that, if the processes are entirely optical the absorption band is narrower than the luminescence one. The detailed mathematics predicts that for such transitions the absorption and emission bands are Gaussian shaped in terms of the photon energy [18, 19].

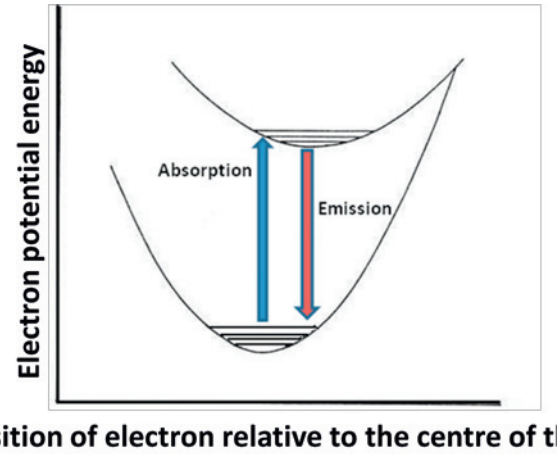

Fig.1. A configurational co-ordinate diagram which relates electron energy and position in the ground and an excited state.

If the initial excitation process is by energy input from a photon the process is termed photoluminescence (PL) and this has a major advantage that energy can be directed into an optical absorption band that is characteristic of one type of site. Hence specific impurity or defect sites can be selected for analysis. Alternatively, photon energies above the band gap can reorganize electrons between many types of site. The depth of excited material is defined by the absorption coefficients of the exciting light and so the penetration into the surface is a function of the absorption spectrum. Luminescence resulting from input energy delivered via an electron beam is termed cathodoluminescence (CL). This is useful as it is often the by product of processes such as imaging with a scanning electron microscope. Hence spatial and spectral data are directly correlated. In terms of depth the signals are primarily from the near surface, even though some electrons will penetrate deeper into the material. A first estimate of the range is that an electron penetrates ~1 micron per 10 keV in unit density material. In complete contrast excitation with X-rays will involve the entire crystal (or glass). This is termed Radioluminescence (RL).

The luminescence spectra that are recorded must be viewed with some caution as there will be self absorption of the light emitted within the material and in most cases emission spectra measured from front, rear and side faces may all differ. If the emission bands occur in regions of absorption of the insulator then the recorded spectra are distorted and corrections for this rarely seem to be discussed. With strong self absorption a single Gaussian emission band can also appear with a central dip which may at first be interpreted as a pair of emission bands.

Despite these uncertainties from experimental artefacts, luminescence has some very positive features. Firstly it is a simple and direct technique and the signals can be spectrally resolved. This is valuable as each type of emission site, whether impurity or structural defect, will have a different emission spectrum; different decay lifetime, and different temperature dependence. The sites are often sensitive to the rate of energy deposition so again this can be

used as a parameter to probe the various component features. Emission is very sensitive not just to the immediate structure of the emission site, but also the long range interactions with neighbouring ions. In particularly detailed studies there are reports of discrimination with changes in spectra over each of say 50 neighbouring shell distances [20, 21]. Consequently the spectra respond to the presence of defects, stress, electric field, impurities, impurity concentration and inclusion of different phases or nanoparticles etc. The sensitivity is excellent and in many cases one can sense such variations down to the parts per billion (ppb).

Such extreme sensitivity is both a bonus and a problem as it implies that every sample will differ to some extent if there is a detailed luminescence analysis, however it offers an excellent tool for materials science to quantify differences between samples from different production batches, or different manufacturers. It also means that the changes in starting material cause alternative responses to heat treatments and radiation. This is valuable design information for structural materials that are to be used in say fusion or fission reactors or with radiation processing. Equally, the changes in spectra are routinely used to indicate the presence of different minerals and phases within geological materials. In biological materials there is also the certainty that healthy and diseased tissue will differ in some aspects of their luminescence sensitivity and response (hence the interest in luminescence for optical biopsy) [22, 23].

2. Particular advantages of IL

Ion beam excitation of luminescence (IL) offers some advantages and complements each of these preceding methods, although in terms of data collection and processing the problems of re-absorption and spectral differences depending on the viewing direction, or detector performance will be the same. For light ions the bulk of the energy is transferred via electronic excitation and the mechanism therefore resembles cathodoluminescence. However there is a major difference in that with IL one can vary the ion energy and mass to change the depth profile of the excitation process. This means that the data are not dominated by the very near surface responses. Since many materials differ in composition and stress at the surface from their interior properties one can vary the ion energy to monitor the IL of these changes. Figure 2 sketches the pattern of energy deposition (dE/dx) for CL and examples of IL for the lightest of ions (H^+) where the IL and CL are most similar. Note that the absolute rate is often higher for the IL. The electronic energy deposition pattern for more energetic heavy ions offers even higher rates of excitation deeper into the material. Such ions beams are frequently described as SWIFT.

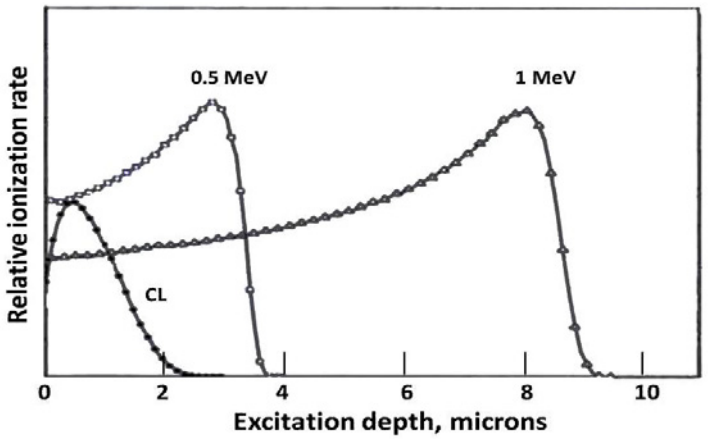

Fig. 2. A comparison of the ionization energy deposition for electron and proton beams in silica. Note the CL rate has been magnified 100 times relative to the IL.

Neither CL nor IL are perfect probes as the act of excitation with ionisation will move electrons between different types of defect site and these can both alter the optical absorption as well as the luminescence properties. In a few materials, most familiarly the alkali halides, the ionisation will even create new defect structures. For more stable materials, such as sapphire or MgO, this is a minor effect. However, at very high energy deposition rates, as used with heavy ions at high energy (SWIFT) damage appears in the electronic stopping region. Excitation can therefore range from charge redistribution to defect and track production as well as relaxation of the lattice structure in the form of distortions or new crystallographic phases. For example in lithium niobate, Nd:YAG or $Bi_4Ge_3O_{12}$, bond relaxations are enabled by the ionization and the results can be used to make optical waveguides by increasing the refractive index, and/or it can cause the material to relax into new crystalline phases. In all ion implantation the energy transfer at the ends of the track, where the ion velocity has slowed down, results in nuclear displacements. This end of track damage is unavoidable. It may also result in luminescence but the spectrum will include features that differ from the zone of ionization excitation. For ions such as MeV protons the nuclear energy deposition will be a few percent of the total energy input, but for higher masses the nuclear fraction increases.

IL has one key feature that is not available with CL and that is to vary the rate of energy deposition along the ionisation track. Figure 3 emphasises that the luminescence spectra are not independent of either the energy or the ionization rate and the different conditions favour different components of the possible luminescence processes. By contrast CL or RL can only offer a limited view of the various spectra. They are inflexible in terms of changing dE/dx and so they offer a limited view of the possibilities. Note that with say CL one can increase the current density but this changes the input power (and temperature) but dE/dx is not significantly

altered as each electron track is independent, so only a negligible fraction of the material has an enhanced excitation rate.

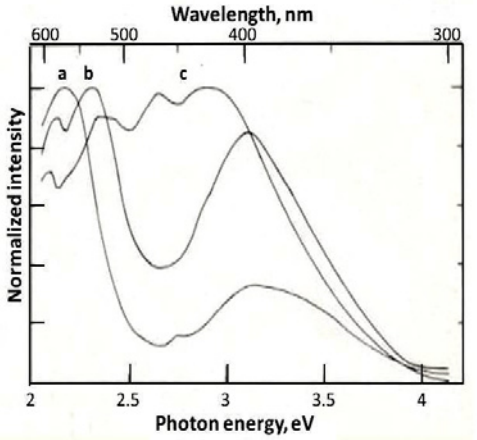

Fig. 3. Ion beams of (a) 1 MeV H^+, (b) 1 MeV He^+ and (c) 2 MeV N^+, have all generated different spectra in NaCl.

Luminescence is inherently sensitive to impurities and, intrinsic defects and therefore thermal history. Changes in emission with dose and dose rate can reveal such variations between samples. A practical example of using IL is shown in figure 4. Here, samples of NaCl from different crystal growers (both marketed as “pure” material with impurities at the ppm level) are contrasted. Not only are the main emission bands appearing in opposite ratios, but the peak values do not coincide, and their dose dependent characteristics are very different. This is suggesting IL is a good diagnostic tool to assess the quality of material, either as supplied, or otherwise processed.

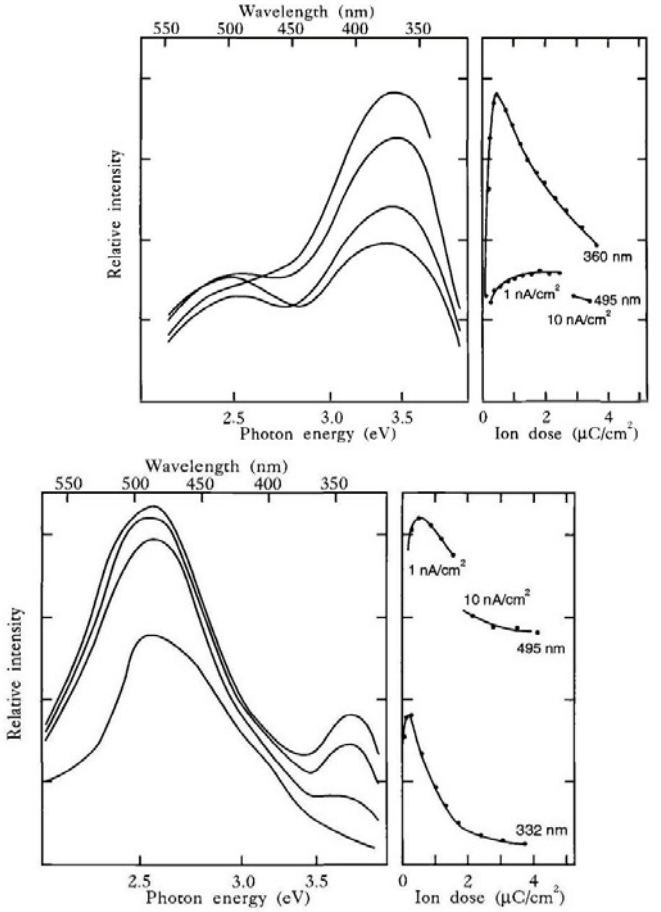

Fig.4. Dose and current density effects for the IL of "pure" NaCl from different suppliers.

Many defect studies have shown that the damage products are sensitive to dE/dx. For example in alkali halides the rate of pair formation (divacancies or di-interstitials) increases with higher dE/dx. Similarly the changes mean we can emphasise the presence of different defect components by varying the dE/dx term if we use different excitation ions. There is also the option to contrast ion and molecular bombardments. This is particularly attractive as the molecules dissociate on impact but the subsequent tracks of the fragments will overlap both temporally and spatially. Hence we can choose energies and beam currents to penetrate the same depth of material with equal input power, but with very different dE/dx conditions. Such features are indicated by figure 5.

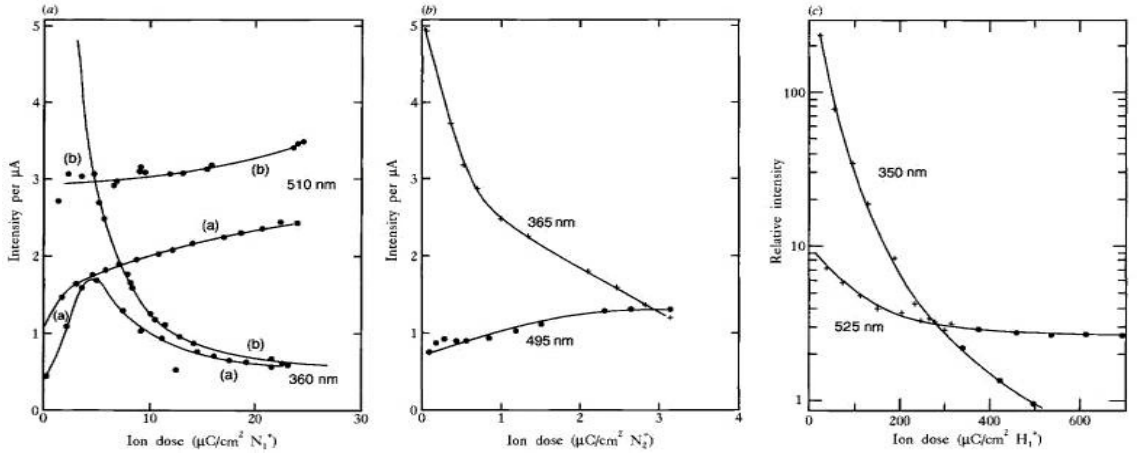

Fig.5. Dose and dose rate effects are seen here for NaCl implanted with nitrogen. (a) 1 MeV N^+ has been used at a current density of (a) 230 nA/cm^2 and in (b) at 16 nA/cm^2.The central figure (b) is for 2MeV N_2^+ irradiation at 0.5 nA/cm^2. (c) is the luminescence data recorded at 77K in which the beam conditions were changed at 300μC from 1 MeV H^+ at 60 nA/cm^2 to 2MeV H_2^+ at half the current. The continuity implies the damage effects shown in figure (c) are from accumulated particle dose and not from dose rate.

Very similar patterns of change are seen with more energetic heavier ions in which different defects, and therefore different emission bands, do not have identical growth behaviour with dose. In the case of a material such as SiO_2 there are crystalline and amorphous variants (quartz and silica) and many related silicates. Nominally the same bands are seen in the luminescence, but with minor variations caused by the structure and dopants. The relevant CL literature is extensive [e.g. 24] but more limited for IL. A recent IL [25] example shows that although the same bands exist in quartz and silica, their relative importance and dose dependencies differ with the structure.

3. Essential additions and future experiments for IL measurements

3.1 Temperature effects Up to the present time most IL data have been collected during very simple steady state excitation and invariably this has been at room temperature. The other approaches (PL, CL or RL) all reveal that variations in temperature can be valuable in distinguishing between different features. This is of course true with IL. The example shown in figure 6 is for H^+ and H_2^+ implants in the mineral chaorite. The results show there is a changing intensity with sample cooling, which is not unexpected, but on varying the dE/dx by moving from H^+ to H_2^+ ion beams two different processes are apparent which have different temperature dependencies. Perhaps this is indicating there are single and pair variants of intrinsic defects.

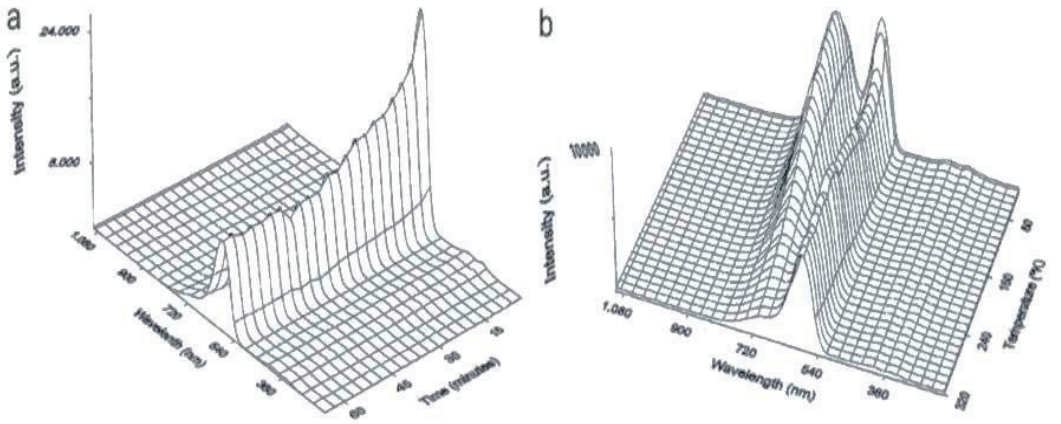

Fig. 6. Ion beam luminescence of chaorite is seen with (a) H^+ and (b) with H_2^+ excitation. Note the molecular beam generates two features with different temperature dependence.

A rather different phenomenon was observed during cooling of albite crystals. The incoming ion beam direction relative to the crystal lattice has a profound influence on the spectra and this varies quite differently with temperature for the two implant directions shown here. For this example the reasons are still speculative, but dose rate effects are clearly apparent. The data of figure 7 are obviously revealing some unexpected new science.

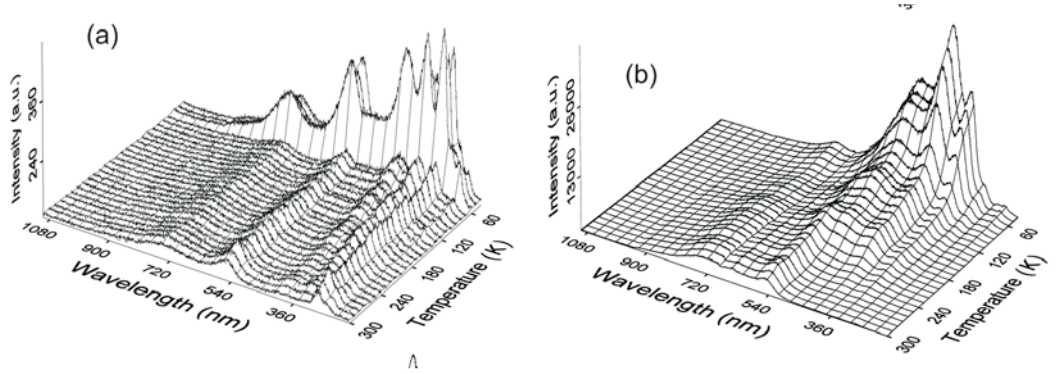

Fig. 7. Ion beam luminescence recorded during heating from 40 to 300 K for two albite orientations.

One possible factor for the albite data may be that the material is being stressed by the directional implant and this is triggering a relaxation into a new structural phase. There have been numerous examples of phase transitions detected by luminescence and in materials such as $SrTiO_3$ and ZnO these were ascribed to a combination of impurities and/or stress. The use of IL to make such characterization has not seriously been explored although the other luminescence literature has been very productive in finding unexpected phase changes. Figure 8 indicates a remarkably clear example of two phase transitions that appear as intensity spikes during the first cooling of KTP crystals. Once cooled the new structural variant does not revert at the transition

temperatures shown in the figure, but instead there is an extreme hysteresis and it requires an annealing at 800°C to regenerate the original material.

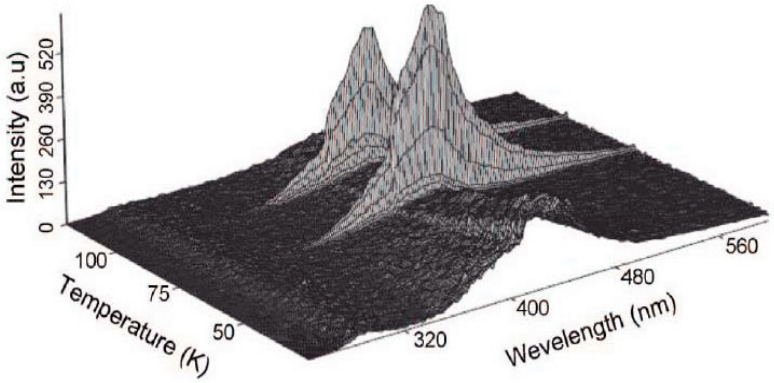

Fig. 8. The emission spectra excited from KTP during the first cooling from room temperature. Note at each phase transition the relaxations favour free electrons and holes that generate the intense emission spikes.

As exemplified by figure 8, luminescence can be surprisingly effective at revealing phase transitions [26]. The effect is not just seen for the host material, but also from transitions of nanoparticle inclusions. This unexpected result arises in part because electronic transition have long range interactions, and probably more crucially from the fact that phase changes of nanoparticles induce stress and pressure effects which extend across large volumes of the host material. Two particularly common examples have been noted from the presence of trapped water and from inclusion of CO_2. The CO_2 example has appeared in studies as diverse as luminescence of optical fibres (where CO_2 can exist in the fabrication process) and in samples of Nd:YAG. The optical fibre data showed an emission peak at 197 K (similar to the pattern seen above for KTP) and 197 K matches the sublimation phase change of CO_2 from solid to gas. A YAG example is shown in figure 9 where the many line features of Nd are excited, but at 197K there is a discontinuity in the blue emission wavelength (and intensity) together with a step change in the lattice parameter of the YAG. Both are consistent with a major pressure change within the crystal. Numerous examples have been noted for trapped gases in other materials with examples linked to Ar, N_2, O_2 etc. So far no effort has been made to us IL to find these trace impurities that are trapped as nanoparticles. There is thus an interesting category of experiments to explore with IL. One suspects that the high excitation and damage component of the IL beams may be particularly successful in stimulating phase changes in materials such as $SrTiO_3$ or SiC where there are metastable phase options that are sensitive to stress and/or defects.

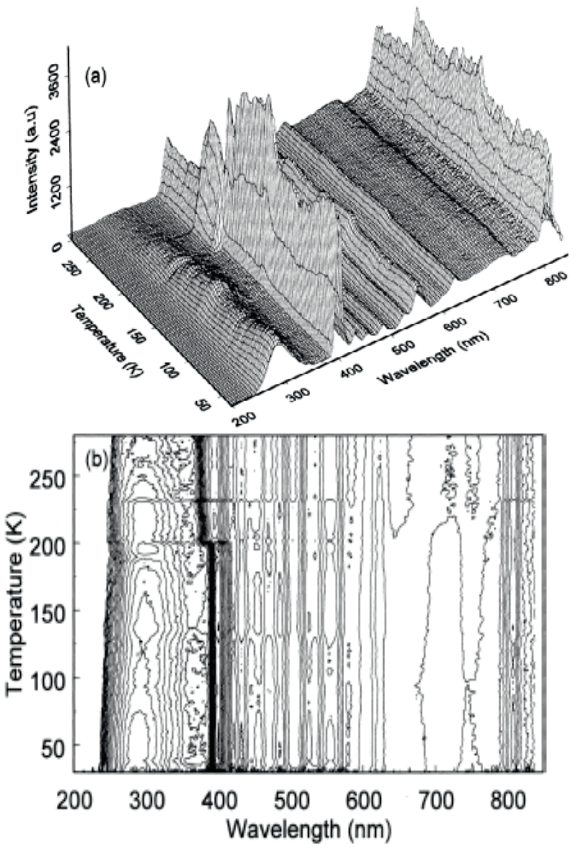

Fig. 9. Emission spectra of Nd in Nd:YAG. There is a discontinuity in wavelength and intensity near 400 nm at 197K. This matches a phase sublimation of CO_2 which is probably trapped in the YAG as nanoparticle bubbles. This emphasises long range pressure effects from the phase change of the inclusions can modify the host signals.

3.2 Lifetime resolution of emission features

Each luminescence site will display decay lifetimes which are characteristic of the site and the temperature of the measurement. Variants of a particular type of defect site can be separated by shifts in spectra and/or by their excited state lifetimes. Such features can be exploited in many contexts. For example in medical imaging of tissue healthy and cancerous tissue will frequently display some similar spectral components but time gated images of pulse excited material can clearly resolve the location of the diseased material. In medical applications this is often termed fluorescence lifetime imaging (FLIM) [27, 28]. For luminescence studies of dopants in crystals and minerals the same method is helpful. Experimentally the equipment must be able to respond to changing spectra on time scales which are faster than the decay lifetimes. Favoured detectors are PM tubes and CCD detectors and the latter are conveniently suited to record wavelength multiplexed spectra. Unfortunately they lack a large dynamic range and even state of the art CCD detectors respond relatively slowly. By contrast the PM tubes can readily resolve changing features down to nanoseconds timescales. This is excellent both for recording time resolved intensity changes following a single pulse excitation, or to record modulated signals with

lock-ion detectors. The weakness is that a normal PM tube can only function with one wavelength at a time. Imaging PM tubes exist and these can be used for lifetime imaging, or for recording transient spectra (e.g. during thermoluminescence). There has been minimal use of lifetime resolved studies for IL and this is definitely an area where new information could readily be obtained. Experimentally one could consider data at a fixed wavelength as a function of time after an ion beam excitation pulse, of lock-in detection as a function of beam scanning across the sample. With photon imaging detectors it is feasible to have both time resolved imaging and/or time resolved spectra. It is thus essential that future exponents of IL introduce such equipment to stay at the forefront of the field.

Figure 10 shows the value of the lock-in amplifier type detection for discrimination between luminescence features of different decay lifetimes. The example here is with CL but the principle has been used in IL examples. On this wavelength plot there are two broad emission bands and evidence of rare earth line spectra in the direct steady state recording, but beam modulation with a square wave excitation (i.e. beam on or off the sample) has rejected the emission at 425 nm. This indicates that the lifetime of the 435 nm band is much longer than for the other features. There have been some effects on the rare earth lines, again implying that they have, as expected, different decay times. There appear to be some shifts in the peak positions but they may have been an experimental artefact.

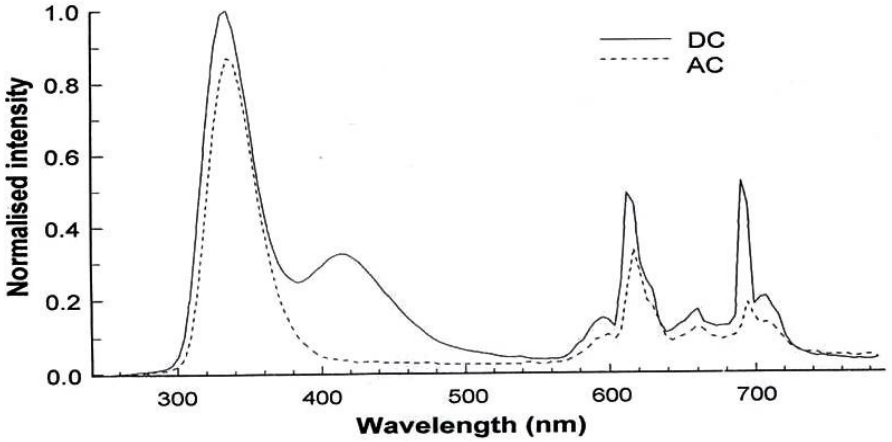

Fig. 10. A comparison of steady state and modulated CL in which higher frequency recording has discriminated against a long lifetime component near 425 nm.

A less obvious advantage of beam modulation is that in many materials the emission features also develop with different lifetimes, and potentially some signals are secondary products of the decay paths of the excitation. Alternatively one may need a high concentration of excited defect states before an emission band is activated. The CL literature of NaCl shows such an example in which the electron beam on/off duty cycle has been varied from the normal 50/50 case to a 5/95 ratio. Figure 11 shows that not only does this alter the relative intensity of the components, but it also shifts the peak positions as different sub sets of processes become dominant. Such an approach has not been exploited greatly with CL and so far has had minimal consideration for IL, although it is a fruitful way to reveal more of the underlying science of the luminescence decay paths and processes.

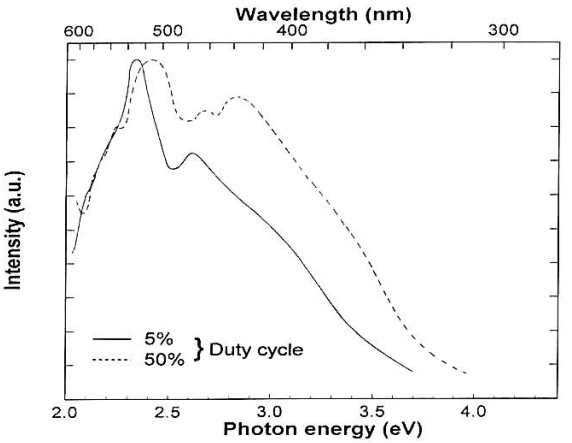

Fig. 11. CL emission from NaCl for modulation duty cycles of 50 and 5%.

3.3 More advanced lifetime experiments

Implantation not only drives electronic transitions which offer luminescence signals, but it also places electronic systems in excited metastable states. There is therefore the opportunity to add further excitation energy to probe these states, either by noting transient absorption or by stimulating additional luminescence features. Such input energy can be via PL or other ionisation type processes from X rays, electrons or synchrotron radiation pulses. Any of these options, or their combinations, can be time gated so that one could track the decay routes and relaxations. As an example the ionisation associated with heavy ion high energy implants not only stimulates luminescence but also induces structural relaxations which decay into defect production. The scale of the track diameter, and the defect density and/or defect association is sensitive to this electronic dE/dx. Hence with pulsed ion beams there is a luminescence signal, but in the presence of a second stimulating source there will be additional features.

There are few cited examples even of CL, PL or RL combinations, but several of the exploratory studies have noted that the double excitations do not yield the sum of the two separate processes. There are further implant conditions which could respond effectively to the double excitation. In both $SrTiO_3$ and ZnO there is evidence that surface implants can trigger changes throughout the bulk of the crystal (probably by stress or electric fields). Measurement of say the line spectra of rare earth dopants in the bulk, or the unimplanted face, would respond to changes driven by in the defect formation in the implanted face. Such long range effects are virtually never considered in implantation studies, but stronger evidence and more examples would cause a re-interpretation of what is feasible in an implanted crystal and indeed it may demonstrate that it is a more general feature than had previously been imagined.

4. Cautionary notes on signal processing

With an expansion of luminescence studies for IL by implantation experts one should add a cautionary note that for historic reasons various subsets of work that use luminescence have developed systematic errors (often because it is treated as a tool for use in other disciplines). Processing steps must first remove dark current and background signals from the raw data. Over wide spectral ranges it is necessary to use blocking filters to avoid overlap of second or third order diffraction signals coinciding with the true first order diffraction at longer wavelengths. The scale of this problem can be severe as

many diffraction grating spectrometers as well as PM tube detectors have peak efficiency in the blue region, but fall in performance by the near infra-red. Indeed in one of our more sensitive Sussex systems the true spectral sensitivity at 800 nm was only 1/200th that of the efficiency at 400 nm, whereas the second order diffraction intensity was around 5 % of the blue response. Blocking filters were therefore absolutely essential. The diffraction grating adds a problem that is rarely mentioned which is that the efficiency is not only wavelength dependent, but also polarization dependent [29]. Typically over a range from say 200 to 900 nm the sensitivity for the two polarizations varies by a factor of 8. Inclusion of polarizing filters can therefore generate quite distorted signals. One option is to use a polarizer followed by an optical fibre which randomizes the directions before they enter the spectrometer. Hence the spectrometer response function is constant.

Corrections of the raw data for the overall response of the optics, filters, monochromator and detector are essential and the end result is a spectrum displayed in terms of wavelength (λ) and intensity. Note this is for a fixed bandwidth set by the monochromator/spectrometer so we have I(λ)dλ versus λ. The science is in terms of photon energy and so the data must be transformed to a plot of I(E)dE versus E. This is trivial since E = hc/λ and dE =- hc/λ^2 dλ. Unfortunately such transformation are not always correctly applied and there are numerous articles where data are displayed, or Gaussian deconvolution fits have been attempted, with {I(λ)dλ versus λ} or with {I(λ)dλ versus E}. Such mistakes produce misleading intensity values, errors in the true peak positions and the wrong number of component peaks [30].

The need for a correct application of response functions is indicated in the three parts of figure 12. The figure commences with (A) a view of 4 equal intensity emission bands in the energy plot, this is followed (B) by the view that would have appeared in the system corrected wavelength domain data. Note that energy and wavelength plots show the peaks in reverse order (e.g. 5.5 eV corresponds to 225 nm). The final plot (C) shows how the raw data might have looked prior to the corrections for the PM and spectrometer response. A more complex variant of (C) would apply for a CCD detector instead of a red sensitive PM tube as the CCD response usually contains several peaks. At first sight such structure may be mistaken for peaks in the emission spectra.

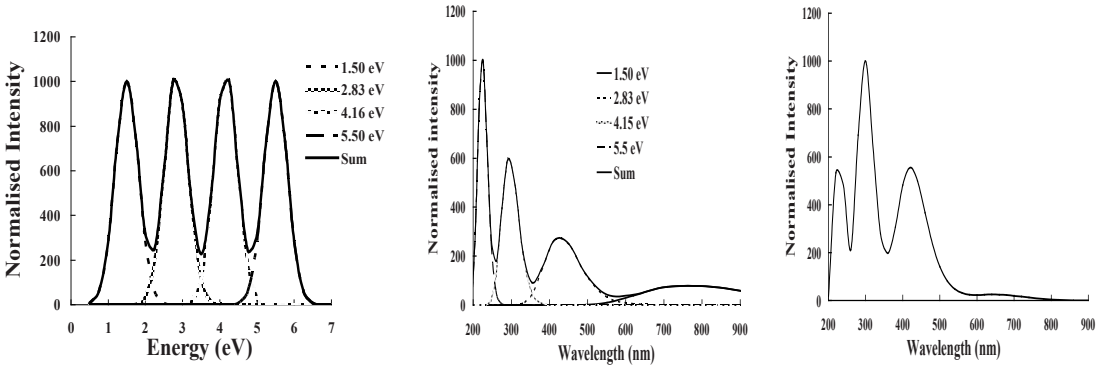

Fig.12. (A) 4 Gaussian peaks of equal intensity and band width, (B) the same peaks in the wavelength domain and (C) a typical example of the raw data before correction for the grating and PM detector responses.

The three views of the data elicit quite different impressions as to the dominant features. Closer inspection of the values also shows that the energy equivalent values of the peaks from the three plots are not the same and so it is not even appropriate to use the wavelength plot and then cite the peak values in energy terms. This peak movement is caused by the $1/\lambda^2$ term in the transformation A to B and it is most obvious for the longer wavelength features. The grating and PM responses also skew the data to shorter wavelengths. Overall for this example the true peak near 827 nm (1.5 eV) moves towards 770 nm (1.61 eV) in figure B to 650 nm (1.91 eV) in figure C. Such transformation errors and inherent differences between systems make inter-comparisons of data extremely difficult and certainly obscure the fine detail that is obtainable with luminescence.

5. Final comments

The preceding article has been based on a presentation at the September 2012 meeting of "Modification and analysis of materials for future energy sources". The choice of examples is therefore somewhat biased in favour of examples from personal collaborations. It is also appropriate to say that I have made many of the data processing errors discussed here and in hindsight I realise some are present in my older references. It is a measure of the robustness of luminescence techniques that despite such problems one can still gain useful insights. In no way does it imply such errors should be tolerated in future research as computer data acquisition and processing can readily avoid these processing errors.

More importantly I have tried to indicate that IL is an extremely powerful and sensitive probe of materials quality and is responsive to impurities, heat treatments and radiation damage. The IL data will help in equipment design as well as insights into mechanisms of implantation and defect creation. There are several areas where current IL equipment is often inferior in terms of flexibility and processing power compared with CL or PL. All the luminescence techniques offer complementary information but IL is under exploited and needs experimental effort to benefit from areas such as the informative lifetime and temperature data. Once routinely introduced IL will be an even more attractive analytical probe.

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